

(11)Publication number : **05-330824**

(43)Date of publication of application : **14.12.1993**

(51)Int.Cl.

C01G 23/00

(21)Application number : **03-116889**

(71)Applicant : **TEIKA CORP**

(22)Date of filing : **19.04.1991**

(72)Inventor : **EGAMI MASAHIRO
ISHIHARA MINORU
TSUBOMOTO NAOTO
KINUGASA MASANORI**

(54) BARIUM TITANATE AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain perfectly spherical barium titanate having high dispersibility while controlling the particle diameter in accordance with the purpose for which the barium titanate is used.

CONSTITUTION: When a titanium compd. and a barium compd. are brought into a hydrothermal reaction to produce barium titanate, perfectly spherical barium titanate having 0.2-5 μ m particle diameter composed of primary particles having 0.005-0.1 μ m particle diameter is produced by adding hydrogen peroxide. Cubic barium titanate or tetragonal barium titanate is obtd. by calcining the resulting perfectly spherical barium titanate. Perfectly spherical denser barium titanate is obtd. by bringing the resulting perfectly spherical barium titanate into a hydrothermal reaction under pressure.

DETAILED DESCRIPTION

[Detailed description]

[0001]

[Field of the Invention] this invention relates to a barium titanate and its manufacture technique.

[0002]

[Prior art] Although a barium titanate is used as a dielectric material of electronic parts, such as a capacitor and a PTC thermistor, recently, from this barium titanate, a particle diameter can be controlled according to the purpose, and to be high dispersibility has come to be demanded.

[0003] For example, although niobium and cobalt are added to a tetragonal barium titanate, the crystal structure of a tetragonal barium titanate is changed from the grain boundary of a ceramics towards the inside of a grain and the so-called core-shell sintered

compact has been obtained in order to obtain the good capacitor of the temperature characteristic of a high dielectric constant system if a capacitor is described, in order to obtain what has a good property, the particle diameter of a ceramics is 0.5-1 micrometer, and it is required for the particle diameter to be complete. In order to obtain such a ceramics, it is required that the barium titanate used as a raw material is also 0.5-1 micrometer, and its particle size distribution of a particle diameter are narrow.

[0004] Moreover, in a high dielectric constant system multilayer ceramic capacitor, although it is making a dielectric ceramic layer thin and the enhancement in capacitor capacity and the miniaturization of a capacitor are achieved, in order to obtain the ceramic layer with a sufficient withstand-voltage property in this case, the particle diameter of particle size distribution is narrow at 0.2-1 micrometer, and the good barium titanate of dispersibility is needed.

[0005] Furthermore, although the PTC thermistor which has a semiconductive ceramic capacitor and the positive temperature characteristic is a device using the electrical property of the grain boundary of a ceramics, in these, it is said that what has a good property has a uniform grain-boundary layer thickness, and a particle diameter becomes complete. Therefore, also in these devices, in order to obtain what has a good property, the barium titanate used as a raw material is 1-5 micrometers of particle diameters, and the narrow thing of particle size distribution is needed.

[0006] However, in the barium titanate manufactured by old technique, it was not fully able to respond to the above-mentioned demand.

[0007] Namely, although the barium titanate was manufactured by the manufacture technique of the conventional barium titanate by carrying out mixed baking of a titanium compound and the barium compound, and making solid phase reaction cause When based on such solid phase reaction, the particle diameter of the barium titanate obtained becomes large on the relation which reacts at an elevated temperature. Since a particle diameter does not become small, particle size distribution were large, control of a particle diameter was not moreover able to be performed and a configuration was not fixed, either, even if it carries out mechanical trituration, dispersibility was bad and was not able to respond at all to the above-mentioned demand.

[0008] Then, in order to solve this problem, manufacturing a barium titanate with a wet method is proposed. For example, the manufacture technique of the barium titanate by the hydrothermal method or the alkoxide method is proposed by the Provisional-Publication-No. 31345 [61 to] official report.

[0009] However, such technique can obtain only the barium titanate of a particle, but has the fault that moreover what has an oval particle shape, the thing to which grain met arise. Therefore, a particle diameter was not able to obtain the good barium titanate of the dispersibility controlled by the target particle diameter in 0.2 to 5 micrometers by such technique.

[0010] Furthermore, when temporary quenching of the false cubic barium titanate obtained by the wet method from the first when carrying out temporary quenching of the tetragonal barium titanate obtained by the solid phase technique although it must be the thing of tetragonal system as a barium titanate used for a core-shell sintered compact was carried out and it obtained a tetragonal barium titanate, since the sintering between grain was [that growth of grain arises unevenly] intense, particle size distribution were not able to become large, and it was not able to respond [as opposed to / the above-

mentioned demand / simply].

[0011]

[Object of the Invention] As mentioned above, the conventional barium titanate had the problem that a particle diameter is fully uncontrollable, and dispersibility was also bad and could not fully respond to the demand based on a miniaturization of electronic parts, such as a capacitor and a PTC thermistor, and highly-efficient-izing.

[0012] Therefore, this invention aims at being able to control to the particle diameter according to the purpose, and offering the barium titanate of high dispersibility.

[0013]

[The means for solving a technical problem] In order to control the particle diameter and configuration of a barium titanate, as a result of repeating a research variously, when this invention persons manufacture a barium titanate at the wet reaction of a titanium compound and a barium compound, by using a hydrogen peroxide, the true sphere-like barium titanate which can control a particle diameter arbitrarily was obtained, and they find out that the above-mentioned purpose is easily attained by it, and came to complete this invention.

[0014] that is, the primary particle of the minute barium titanate whose particle diameter of the barium titanate of this invention is 0.005-0.1 micrometers is the true spherical barium titanate whose particle size distribution which were boiled and carried out flocculation combination firmly are 0.2-5 micrometers of narrow particle diameters spherically [true], and when this true spherical barium titanate carries out the wet reaction of a titanium compound and the barium compound using a hydrogen peroxide, it comes to be obtained

[0015] in the wet reaction of the above-mentioned titanium compound and a barium compound, a hydrogen peroxide advances the generation reaction of a barium titanate slowly -- making -- it -- a grain form -- it is thought that it becomes the factor which makes the narrow true spherical barium titanate of particle size distribution generate by 0.2-5 micrometers of the particle diameters which the primary particle of the barium titanate which is 0.005-0.1 micrometers true-spherical-boiled, and condensed

[0016] And the primary particle of a barium titanate is carrying out flocculation combination of the barium titanate of the shape of this true sphere firmly, and by handling operation at the time of a manufacture of electronic parts, such as a capacitor and a PTC thermistor, it does not collapse and is considered the primary particle of a barium titanate not only is condensing physically, but that has produced a kind of chemical combination.

[0017] And the particle diameter of the barium titanate obtained is arbitrarily controllable by changing the reaction condition of a wet reaction etc.

[0018] Thus, although it can be used as it is as the raw material of electronic parts, such as a capacitor and a PTC thermistor, i.e., a raw material of electroceramics, the obtained true spherical barium titanate carries out temporary quenching of this, and it can change crystal form into a cubic or a tetragonal phase, and let it be the more desirable electroceramics raw material which is easy to control from the grain form of a ceramics, or a grain boundary's.

[0019] Namely, although crystal form changes from a false cubic to a cubic or a tetragonal phase, and crystallinity is good and becomes what it is easy to control from the particle diameter of a ceramics, or a grain boundary's as mentioned above by carrying out

temporary quenching above 600 degrees C, the above-mentioned true spherical barium titanate. These cubics or a tetragonal barium titanate, the true spherical barium titanate before temporary quenching -- literally -- true -- since it is spherical and there are few contacts between grain, there are few sinterings by temporary quenching, the particle diameter of the true spherical barium titanate before temporary quenching is maintained mostly, particle size distribution are narrow and dispersibility is excellent.

[0020] Moreover, if the above-mentioned true spherical barium titanate is made to react again under pressurization (hydrothermal reaction), a more precise true spherical barium titanate shall be obtained and it shall be easy to control from the particle diameter of a ceramics, or a grain boundary's.

[0021] Furthermore, in this invention, in case a true spherical barium titanate is manufactured, the true spherical barium titanate which contains different particle-diameter grain or different composition grain inside can be obtained by putting in the barium-titanate grain of a parvus particle diameter, or the grain of other perovskite type compounds from the particle diameter of a true spherical barium titanate made to generate as a crystalline nucleus.

[0022] Since the different particle-diameter grain or different composition grain contained inside such a true spherical barium titanate raises the electrical property of a ceramics or promotes the crystalline enhancement in the grain by baking or temporary quenching, it becomes the factor which raises the property of a true spherical barium titanate more.

[0023] The [reaction raw material] and the [reaction technique] of next using it in manufacturing the true spherical barium titanate of this invention are explained in detail.

[0024] In this invention, a titanium compound and a barium compound are used as a reaction raw material about a [reaction raw material], and a hydrogen peroxide is used at the time of a reaction. Then, it is as follows when it explains in the order of a titanium compound, a barium compound, and a hydrogen peroxide.

[0025] Although it can be used, without receiving a constraint especially if a barium compound and perovskite type barium titanate is generated as a titanium compound, what melts in the aqueous solution of a hydrogen peroxide partially, or is melted completely is desirable, and what does not contain a component for which it mixes in the barium titanate to generate and the property is reduced as much as possible is desirable.

[0026] Instantiation of a desirable titanium compound raises organic titanium compounds, such as inorganic titanium compounds, such as titanium oxide and hydroxylation titanium, and oxalic acid titanium, a titanium alkoxide, from the above viewpoints, for example.

[0027] industrial -- an acquisition -- easy titanium oxide and hydroxylation titanium are used abundantly. And when using hydroxylation titanium, it is desirable to measure the ignition loss, to find the weight of the titanium oxide in hydroxylation titanium (TiO_2), and to make the titanium oxide weight into the criteria of a quantitative ratio in case of the wet reaction with a barium compound from the viewpoint of business. In addition, in measurement of ignition loss, it is suitable on the basis of heating at 1000 degrees C for 2 hours.

[0028] Although it can be used, without receiving a constraint especially if it reacts with the above-mentioned titanium compound and a perovskite type barium titanate is generated as a barium compound, a basic barium compound is usually used.

[0029] Moreover, what does not contain a component for which it mixes in the barium titanate to generate and the property is reduced as much as possible is desirable, and the alkoxide of a barium hydroxide, a barium oxide, and barium etc. is raised from such a viewpoint as a desirable barium compound, for example.

[0030] although various kinds of things can be used especially as a hydrogen peroxide, without being limited, commercial 30% (weight %) and the following -- the same) hydrogen peroxide solution, 35% hydrogen peroxide solution, 50% hydrogen peroxide solution, 60% hydrogen peroxide solution, etc. are usually used from an acquisition, the ease of handling, etc.

[0031] Although there is especially no limit about the addition sequence of these titanium compounds, a barium compound, and a hydrogen peroxide about the [reaction technique], before adding a barium compound except for the case where it reacts by thin concentration, it is desirable to mix and to make a titanium compound and a hydrogen peroxide react. That is, when a hydrogen peroxide is added except for the case where it reacts by thin concentration, in the system in which a barium compound exists, it is because the barium oxide (BaO_2) of poor solubility generates, precipitation arises and it becomes impossible to use it for a reaction.

[0032] As for the amount of the hydrogen peroxide used, 0.1-10 are desirable at TiO_2 , the mole ratio 2, i.e., H_2O_2 , of the hydrogen peroxide to a titanium compound (however, it converts into titanium oxide) /2 (mole ratio).

[0033] Even if the amount of a hydrogen peroxide exceeds and uses 10 by the mole ratio to the above-mentioned titanium compound, the increase in an effect is not seen, but it is only uneconomical to decompose at the time of the reaction with a titanium compound. Moreover, when fewer than 0.1, it fully stops acquiring the effect by addition of a hydrogen peroxide by the mole ratio [as opposed to the above-mentioned titanium compound in the amount of a hydrogen peroxide].

[0034] If a titanium compound and a hydrogen peroxide are mixed, usually, it will react, and the peroxide of titanium will be produced and yellowed. It can also be used as a suspension solution which could perform this reaction completely, and could use it as full lysis aqueous solution of the peroxide of titanium, and produced the peroxide of titanium.

[0035] For example, if a hydrogen peroxide is mixed 3 or more times by the mole ratio to titanium when [thin] the titanium oxide conversion concentration in a hydroxylation titanium slurry is 0.05-0.25 mols/about l, it will become the full lysis aqueous solution of the peroxide of titanium.

[0036] However, a deep case so that the titanium oxide conversion concentration in a hydroxylation titanium slurry may be one mol/l., and when crystalline titanium oxide is used irrespective of concentration, however it may change the amount of a hydrogen peroxide, it does not become the full lysis aqueous solution, but becomes a suspension solution. However, even if it is the full lysis aqueous solution of the peroxide of the above titanium and it is a suspension solution, it is convenient for manufacturing a true spherical barium titanate.

[0037] Although ordinary temperature is sufficient as the temperature at the time of mixture of a hydrogen peroxide, in order to obtain comparatively the full lysis aqueous solution or the suspension solution of a peroxide of homogeneous titanium for a short time, it is desirable to heat at 40-100 degrees C.

[0038] As titanium oxide conversion concentration of a titanium compound, it is in the

status which added the barium compound, and 1. is [1.] especially desirable in 0.06-1 mol / 0.01-2.5 mols /. If the above-mentioned concentration exceeds 1. in 2.5 mols /, it will be in the status with it difficult [for viscosity to stir highly], and the barium titanate which reacts with a barium compound and is obtained will become what has an uneven particle diameter. When the above-mentioned concentration is lower than 1. 0.01 mols /, a conversion falls remarkably.

[0039] Moreover, the reaction with a barium compound is preceded and 0.01 - 10% of a trace element, nonmetals, or those compounds may be added as an improvement of the property in the case of electroceramics-izing, or an additive for sintering acids.

[0040] thus, the mole ratio [as opposed to titanium to the obtained full lysis aqueous solution or the suspension solution of a peroxide of titanium] of barium, i.e., Ba/Ti, (mole ratio) -- 0.8-10 -- it adds, and it mixes uniformly and a barium compound is made to react so that it may be preferably set to 1-3

[0041] In this case, although a titanium compound and a barium compound react and the perovskite type barium titanate of a false cubic generates, in order to obtain a true [which is 0.2-5 micrometers] spherical [the particle diameter of a primary particle / at 0.005-0.1 micrometers / the particle diameter of an aggregated particle] barium titanate, it is desirable to set up the mole ratio of titanium and barium, the concentration of a barium compound, reaction temperature, etc. so that the generation reaction of a barium titanate may not be completed desirably less than 1 hour within 4 hours.

[0042] And in order to arrange the particle diameter of the true spherical barium titanate obtained and to narrow particle size distribution, it is desirable to perform mixture with a titanium compound and a barium compound at the temperature below the temperature which a reaction starts.

[0043] Furthermore, it is desirable between the temperature which a reaction completes in 4 hours, and temperature lower 40 degrees C than the temperature desirably to carry out a digestion reaction 1 hour or more desirably 0.1 hours or more between the temperature which the reaction of the above-mentioned titanium compound and a barium compound completes in 4 hours, and temperature lower 50 degrees C than the temperature. And it is desirable to make it react above the temperature which a reaction completes in 4 hours, and to complete a reaction after a digestion reaction. In addition, even if it continues a reaction more than it as the above-mentioned reaction is completed, the integrated intensity of the barium titanate by X-ray diffraction says the status that it stopped changing on the parenchyma.

[0044] Usually, 40-100 degrees C of digestion reactions are preferably performed at 60-100 degrees C. This digestion reaction is performed under an ordinary pressure or reduced pressure. For example, if it carries out where this digestion reaction is pressurized using an airtight container, the grain which is not spherical will enter, the barium titanate obtained will become the large thing of particle size distribution, even when it is easy to become a particle 0.1 micrometers or less and it is set to 0.2 micrometers or more, and a 0.2-5-micrometer true spherical barium titanate like this invention will not be obtained. When carrying out the pressurization reaction especially of this inclination above 100 degrees C, it becomes remarkable.

[0045] In addition, it is desirable that the flow of the nitrogen is carried out into the system of reaction, and a barium compound and components, such as carbon dioxide gas in air, are made not to react among a reaction.

[0046] Although the true spherical barium titanate of 0.2-5 micrometers of the particle diameters which consisted of a primary particle of 0.005-0.1 micrometers of particle diameters as mentioned above is obtained, in this invention, it is making for the particle diameter of a primary particle to be $1/3$ or less [of the particle diameter of a true spherical barium titanate] into requirements between the particle diameters of the true spherical barium titanate which is the particle diameter and aggregated particle of this primary particle. This is because true **** is spoiled and it stops obtaining the good true spherical barium titanate of dispersibility, when the particle diameter of a primary particle becomes larger than one third of the particle diameters of the true spherical barium titanate which is an aggregated particle. It is desirable that especially the particle diameter of a primary particle is $1/5$ or less [of the particle diameter of a true spherical barium titanate].

[0047] Moreover, in this invention, although the particle diameter of a true spherical barium titanate is specified as 0.2-5 micrometers, this is based on the following ground. That is, the dispersibility to a binder is bad at the time of molding before a parvus case has bad dispersibility, for example, a particle diameter ceramics-izes from 0.2 micrometers, and a uniform Plastic solid is hard to be obtained at it. It becomes impossible that moreover, it is adapted for flowing of thin-film-izing of electronic ceramic parts, such as a capacitor and a PTC thermistor, and a miniaturization when a particle diameter becomes larger than 5 micrometers.

[0048] Furthermore, in this invention, although it is making for the particle diameter of a primary particle to be 0.005-0.1 micrometers into requirements, this is based on the following ground. That is, if the diameter of a primary particle is not obtained by the parvus thing with a wet method from 0.005 micrometers and the diameter of a primary particle becomes larger than 0.1 micrometers, the temperature at the time of performing baking and temporary quenching will become high, and it will become difficult to obtain the good barium titanate of the dispersibility with few sinterings.

[0049] Below, an example is met and the factor which controls the particle diameter and particle shape of a barium titanate is explained in detail. For example, the slurry whose titanium oxide concentration is 0.312 mols/l. is obtained using the hydroxylation titanium cake obtained by hydrolyzing the aqueous solution of a titanium tetrachloride with aqueous ammonia. To it, hydrogen peroxide solution is added to this slurry by $H_2O_2 / TiO_2 = (\text{mole ratio}) 6.35$, and it mixes, it stirs at 60 degrees C for 2 hours, and a suspension solution is obtained.

[0050] The temperature of this aqueous solution is lowered to 40 degrees C, and it adds and mixes so that a barium hydroxide and 8 monohydrate may be set to $Ba/1.4$ in this aqueous solution by Ti (mole ratio). After mixture, stirring, a digestion reaction is performed at 70 degrees C for 2 hours, and the true spherical barium titanate of 1 micrometer of mean particle diameters is obtained by reacting at 100 degrees C after that for 4 hours.

[0051] First, the influence affect the particle diameter and particle shape of barium-titanate grain of a solution is explained, quoting the above-mentioned example of a reaction. [of concentration]

[0052] A particle diameter tends to become small so that the concentration, especially barium ion concentration of a solution become high.

[0053] this example of a reaction -- setting -- $Ba/Ti(\text{mole ratio}) = 1.4$ -- since barium ion

concentration will increase in connection with it if the titanium oxide conversion concentration in a solution turns into concentration higher 0.312 mols /than 1. if it is fixed, the particle diameter of a barium titanate becomes smaller [the above-mentioned example of a reaction] than 1 micrometer Conversely, if titanium oxide conversion concentration turns into low concentration from 1. in 0.312 mols /, since barium ion concentration will decrease in connection with it, a particle diameter becomes larger than 1 micrometer.

[0054] Moreover, the particle diameter of a barium titanate becomes small so that temperature is high, and as for the reaction temperature of a titanium compound and a hydrogen peroxide, the particle diameter of a barium titanate becomes large so that temperature is low.

[0055] Although the slurry and hydrogen peroxide of a titanium compound are mixed and the full lysis aqueous solution or the suspension solution of a peroxide of titanium is specifically produced, the solution is aged at 20-100 degrees C after mixing the slurry and hydrogen peroxide of a titanium compound in that case. A particle diameter will become large if a particle diameter will become small if this aging temperature becomes high, and aging temperature becomes low.

[0056] Since barium ion concentration increases so that the ratio becomes large about Ba/Ti (mole ratio), the particle diameter of a barium titanate tends to become small.

[0057] In the aforementioned example of a reaction, although the amount of a barium compound is set to Ba/Ti(mole ratio) =1.4, if it is made [more] than it, barium ion concentration will increase, a reaction rate becomes quick, and although a particle shape does not change, a particle diameter becomes small. however -- for example, Ti (mole ratio) exceeds Ba/10 -- extremely, under presence of superfluous barium ion, a barium titanate does not become a floc any longer, but a particle generates it

[0058] A particle diameter becomes large, although barium ion concentration will decrease and a particle shape will not change, if the amount of a barium hydroxide is made fewer than Ba/Ti(mole ratio) =1.4. It corrects, for example, the reaction itself does not happen any longer under presence of the barium ion with little Ba/Ti (mole ratio) out of less than 0.8.

[0059] However, if Ba/Ti (mole ratio) is made to become 0.8 or more by the time of a reaction end even if Ba/Ti (mole ratio) is less than 0.8 temporarily, a true spherical barium titanate can be made to generate.

[0060] A particle diameter becomes large so that a prolonged digestion reaction will be carried out near [which a titanium compound and a barium compound react and a barium titanate begins to generate] temperature, if the influence affect the particle diameter of digestion reaction temperature is described below. Moreover, a particle diameter becomes small so that digestion reaction temperature becomes high.

[0061] for example, the barium titanate which carries out the temperature up of the barium titanate obtained if the digestion reaction of carrying out a digestion reaction at the digestion reaction in temperature lower than 70 degrees C, for example, 50 degrees C, for 2 hours etc. is carried out and it carries out a temperature up to 100 degrees C after that at the temperature to which a reaction rate becomes extremely slow as quickly from 20 degrees C to 100 degrees C as possible, carries out a digestion reaction at 100 degrees C, and was obtained -- the same -- 0.6 micrometers of mean particle diameters -- it true-spherical-comes to That is, since the same result is brought even if it does not carry out

the digestion reaction in the low temperature to which a reaction does not progress, either, it will become meaningless.

[0062] A particle diameter becomes small, although a reaction rate will increase and a particle shape will not change, if a digestion reaction is carried out at temperature higher than 70 degrees C. For example, if an airtight container is used and digestion reaction temperature is made high to about 180 degrees C, a reaction rate will become quick too much and all the barium titanates that already become unable to maintain a particle shape which forms a floc, and are obtained will become a particle.

[0063] Moreover, digestion reaction temperature is made lower than the case of the aforementioned example of a reaction, and digestion reaction time is lengthened, after having carried out the temperature up and carrying out a digestion reaction over 10 hours from 60 degrees C to 70 degrees C, when it makes it react at 100 degrees C for 4 hours and a reaction is completed, the particle diameter of the barium titanate obtained becomes larger than the case of the aforementioned example of a reaction, and a mean particle diameter is set to 2.5 micrometers.

[0064] By above reaction raw materials and reaction technique, the narrow true spherical barium titanate of particle size distribution of 0.2-5 micrometers of the particle diameters which consisted of a primary particle of 0.005-0.1 micrometers of particle diameters is obtained.

[0065] the obtained true spherical barium titanate -- usually -- rinsing, acid treatment, etc. -- Ba/Ti (mole ratio) -- 0.95-1.05 -- it is preferably used by being adjusted to 0.99-1.02

[0066] the above-mentioned true spherical barium titanate -- a configuration -- true -- since the particle diameter is arbitrarily controllable by dispersibility being excellent and selecting digestion reaction temperature, the concentration of a titanium compound, Ba/Ti (mole ratio), etc., since it is spherical, it can control to the particle diameter according to the purpose accompanied by a miniaturization of electronic parts, such as a capacitor and a PTC thermistor, and highly-efficient-izing, and can fully correspond to demand that it is high dispersibility

[0067] Next, the 0.2-5-micrometer true spherical barium titanate which consisted of a primary particle of the 0.005-0.1 micrometers of the above-mentioned particle diameters [The cubic barium titanate and tetragonal barium titanate] which carry out temporary quenching and are obtained, The 0.2-5-micrometer true spherical barium titanate which consisted of a primary particle of the 0.005-0.1 micrometers of the above-mentioned particle diameters inside [which applied the [precise true spherical barium titanate which is made to react again and is obtained under pressurization], and this invention] [different grain type grain or different composition grain True spherical barium-titanate] to contain is explained.

[0068] Although it can be used as a raw material of electroceramics even if the true spherical barium titanate obtained by the cubic barium titanate which carries out temporary quenching and is obtained, and the [tetragonal barium-titanate] this invention remains as it is, it is the thing of the status that the primary particle condensed, and crystal form is a false cubic.

[0069] Then, if temporary quenching of this is carried out above 600 degrees C, crystal form changes to a cubic or a tetragonal phase, crystallinity will be good and the barium titanate which is easy to control from the particle diameter of a ceramics or a grain boundary's will be obtained.

[0070] For example, if temporary quenching of this true spherical barium titanate is carried out at 600-1100 degrees C, the spherical barium titanate of the good cubic of the dispersibility with few sinterings which maintained the particle diameter and configuration of a true spherical barium titanate, or a tetragonal phase will be obtained.

[0071] Moreover, if temporary quenching is carried out at 900-1300 degrees C, a tetragonal barium titanate will be obtained. In this case, it will become spherical, if temperature is low and a particle diameter is large. And if a particle diameter is small or carries out temporary quenching at an elevated temperature, it will become rectangular parallelepiped-like single crystal powder.

[0072] By the above temporary quenching, a barium titanate becomes the electroceramics raw material which the particle diameter and a grain boundary tend to control, when it becomes a high-density crystalline good thing and is made into a ceramics.

[0073] and these cubic barium titanates and a tetragonal barium titanate -- the configuration of the true spherical barium titanate before temporary quenching -- literally -- true -- it is spherical, since there are few contacts between grain, there are few sinterings by temporary quenching, therefore the particle diameter before temporary quenching is maintained mostly, particle size distribution are narrow and dispersibility is excellent

[0074] Thus, these cubic barium titanates and a tetragonal barium titanate have high usefulness compared with what carried out temporary quenching of the barium titanate which can control a particle diameter according to the purpose which is the characteristic feature of the true spherical barium titanate before temporary quenching, holds the property of being high dispersibility, and was obtained with the conventional wet method.

[0075] If the 0.2-5-micrometer true spherical barium titanate which consisted of a primary particle of 0.005-0.1 micrometers of the particle diameters of a [precise true [which is made to react again and is obtained under pressurization] spherical barium-titanate] this invention is made to react again under pressurization (hydrothermal reaction), a more precise true spherical barium titanate can be obtained.

[0076] Hydrothermal reaction under such pressurization can be performed to the isolated true spherical barium titanate, and it can also be succeedingly carried out to a manufacture of the true spherical barium titanate under an ordinary pressure, without isolating.

[0077] And when a barium compound is added at the time of the hydrothermal reaction under the above-mentioned pressurization, there is an operation which promotes growth of a primary particle. The true spherical barium titanate such a primary particle grew up to be serves as a suitable raw material, when obtaining the ceramics which has arranged the additive to the grain boundary.

[0078] The barium titanate obtained by the hydrothermal reaction under the above pressurization can also be used, after carrying out temporary quenching and considering as temporary-quenching powder, although it remains as it is and can be used.

[0079] The true spherical barium titanate obtained by the hydrothermal reaction under the above pressurization is more precise, tends to control the particle diameter and grain boundary of a ceramics, and, as a result, can attain more easily the enhancement in a density of a ceramics, the enhancement in a withstand voltage, the enhancement in a mechanical strength, etc.

[0080] The true spherical barium titanate which contained different particle-diameter

grain or different composition grain inside can be manufactured by applying the technique of this invention to a [true [which contains different particle-diameter grain or different composition grain inside] spherical barium-titanate] pan.

[0081] For example, a particle diameter can use the good tetragonal barium titanate of parvus crystallinity from the particle diameter of the generation grain made into the purpose by 0.1 micrometers or more, can use this tetragonal barium titanate as a crystalline nucleus, can apply the technique of this invention, and can manufacture the true spherical barium titanate which contains the tetragonal barium-titanate grain of a different particle diameter inside. And a tetragonal rectangular parallelepiped-like barium titanate can be more easily obtained by carrying out temporary quenching of the true spherical barium titanate which contains tetragonal barium-titanate grain in this interior.

[0082] Moreover, the technique of this invention can be applied, being able to use as a crystalline nucleus the perovskite compound contributed to an improvement of electrical properties, such as a capacitor and a PTC thermistor, from the particle diameter of the target generation grain by elevated-temperature degree of sinterings, such as a strontium titanate of a parvus particle diameter, zirconic acid barium, and titanic-acid zirconic acid barium, and the true spherical barium titanate which contains different composition grain, such as a strontium titanate, zirconic acid barium, and titanic-acid zirconic acid barium, inside can be manufactured.

[0083] And making the different composition grain and the barium titanate which serve as the crystalline nucleus by calcinating the true spherical barium titanate which contains different composition grain in this interior react, it is enabled to carry out a low temperature sintering, and the electrical property of a barium titanate based on the different composition grain of an elevated-temperature degree of sintering can be improved by the low temperature sintering.

[0084] The true spherical barium titanate which contains such different particle-diameter grain or different composition grain inside The different particle-diameter grain or different composition grain of right crystallinity which carries out temporary quenching of the different particle-diameter grain of right crystallinity obtained by the solid phase technique, different composition grain, or the grain obtained with the wet method, and was obtained A titanium alkoxide, the aqueous solution of a titanium salt, or these are added to hydroxylation titanium, titanium oxide, etc. which are obtained by hydrolyzing, and it mixes, and after that, mix, a hydrogen peroxide and a barium compound are made to react, and it is obtained.

[0085] Thus, the true spherical barium titanate containing the different particle-diameter grain or different composition grain obtained with the application of the technique of this invention has the characteristic feature of the true spherical barium titanate of this invention that particle size distribution are narrow and are high dispersibility.

[0086] In a manufacture of the true spherical barium titanate which contains different particle-diameter grain or different composition grain in the above-mentioned interior, you may add directly in a titanium alkoxide or the aqueous solution of a titanium salt, and a hydrogen peroxide may be added after those hydrolysis. That is, before mixing and making a barium compound react, as long as it becomes, you may carry out addition mixture in any phase.

[0087] It is desirable to perform mixture of different particle-diameter grain or different composition grain before hydrolysis of a titanium alkoxide or the aqueous solution of a

titanium salt. It adds before hydrolysis, and by hydrolysis, this makes hydroxylation titanium adhere to those grain front faces, and is based on the ground those different particle-diameter grain or different composition grain can be certainly incorporated inside a barium titanate by the reaction with a barium compound. Moreover, as for different particle-diameter grain or different composition grain, it is desirable to make it fully distribute with wet before mixture.

[0088] It is desirable to use the narrow thing of the particle size distribution acquired by the tetragonal rectangular parallelepiped-like barium titanate which carries out temporary quenching of the true spherical barium titanate of this invention, and was obtained as a tetragonal barium titanate used in a manufacture of the true spherical barium titanate which contains the above-mentioned tetragonal barium titanate inside although not necessarily restrained, the calcinating method, the autoclave method, etc.

[0089]

[Effect of the invention] the true spherical barium titanate of this invention -- the purpose -- responding -- a particle diameter -- being controllable -- and -- true -- it is spherical and dispersibility is excellent

[0090] Therefore, the true spherical barium titanate of this invention can fully correspond to the demand which has come to be required of a barium titanate in connection with a miniaturization of electronic parts, such as a capacitor, a PTC thermistor, and a piezo electric crystal, and highly-efficient-izing "it can control to the particle diameter according to the purpose, and is high dispersibility."

[0091] Although it can be used as a raw material of electronic parts, such as the above-mentioned capacitor and a PTC thermistor, even if the true spherical barium titanate of this invention remains as it is, if temporary quenching of the true spherical barium titanate of this invention is carried out, the cubic spherical barium titanate or tetragonal spherical barium titanate of high dispersibility will be obtained narrowly [there are few sinterings and / the particle size distribution which maintained the particle diameter and configuration of a true spherical barium titanate before temporary quenching].

[0092] Compared with the barium titanate obtained with a conventional solid phase technique and a conventional wet method, since particle size distribution are narrow and are spherical, there are few amounts of air taking at the time of molding, therefore occurrence of a lamination is suppressed, and it is enabled to obtain homogeneity and the high-density-ized Plastic solid, and these spherical barium titanates of the last attainment density of a sintered compact improve sharply.

[0093] Therefore, the capacitor which was excellent in the dielectric characteristics to which the particle diameter was equal can be obtained by using the above-mentioned spherical barium titanate. Furthermore, by carrying out temporary quenching of the aforementioned true spherical barium titanate at an elevated temperature, there are few sinterings and they can obtain the tetragonal rectangular parallelepiped-like barium titanate with narrow particle size distribution.

[0094] Since this tetragonal rectangular parallelepiped-like barium titanate is a high-density barium titanate became tight still better than the above-mentioned spherical barium titanate and controlling the particle diameter and grain boundary of a ceramics strictly can perform it more easily, it can obtain a capacitor, a PTC thermistor, etc. superior to the dielectric characteristics's by using this tetragonal rectangular parallelepiped-like barium titanate.

[0095] Moreover, by carrying out temporary quenching of the true spherical barium titanate which contains the tetragonal barium titanate of a different particle diameter inside, the tetragonal rectangular parallelepiped-like barium titanate to which the particle diameter was still easily equal can be obtained, and a capacitor, a PTC thermistor, etc. which were excellent in the above dielectric characteristics can be obtained more easily.

[0096] Moreover, making a barium titanate and different composition grain react by calcinating the true spherical barium titanate which contains the different composition grain of elevated-temperature degree of sinterings, such as a strontium titanate, zirconic acid barium, and titanic-acid zirconic acid barium, inside, it can be enabled to carry out a low temperature sintering, and electrical properties, such as a capacitor and a PTC thermistor, can be improved more easily.

[0097]

[Example] Below, an example is given and this invention is explained more concretely.

[0098] The example 1 titanium-tetrachloride aqueous solution (Osaka titanium company make, titanium 16, 4% inclusion) was hydrolyzed with aqueous ammonia 5%, obtained hydroxylation titanium gel was filtered and rinsed, and the hydroxylation titanium cake [I] whose titanium oxide concentration is 12.3% in the equivalent weight by ignition loss was obtained.

[0099] This hydroxylation titanium cake [I] 221g of hydrogen peroxide solution was added 30% in the aqueous solution which distributed 200g uniformly 654g of water. It was [mole ratio / ["H₂ O₂ / TiO₂" (mole ratio) shows hereafter] / of a hydrogen peroxide / to the titanium oxide at this time] 6.34. Moreover, the titanium oxide concentration in the obtained slurry calculated 70% of hydrogen peroxide solution with water 30%, and was 0.312 mols/l.

[0100] The obtained slurry was mixed to homogeneity at 60 degrees C for 2 hours, and the suspension solution [II] was obtained. This suspension solution is lowered to 40 degrees C by natural air cooling, and it was made to react for 4 hours, carrying out a temperature up and flowing back to 100 degrees C, in 0.5 hours adding and carrying out the nitrogen flow of the 136g [Ba/Ti(mole ratio) =1.4] of the barium hydroxide and 8 monohydrates to this suspension solution.

[0101] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.63-0.77 micrometers, the barium titanate manufactured by this reaction had narrow particle size distribution, and the mean particle diameter was 0.70 micrometers.

[0102] Drawing 1 is an electron microscope photograph 30,000 times the scale factor of this which shows the particulate structure of the barium titanate manufactured according to this example 1. As shown in this drawing 1 , even when the barium titanate manufactured according to the example 1 is expanded by 30,000 times, the true **** of a particle shape is high, and the particle diameter is also almost uniform, and it turns out [of particle size distribution] that it is narrow.

[0103] hydroxylation titanium cake [produced in the example 2 example 1 -- in the aqueous solution which distributed I]200g uniformly by 217g of water, 820g [H₂ O₂ / TiO₂ = (mole ratio) 10.0] addition of hydrogen peroxide solution was done 30%, and the slurry whose titanium oxide concentration is 0.312 mols/l. like an example 1 was obtained

[0104] The obtained slurry was mixed to homogeneity at 20 degrees C for 2 hours, and the suspension solution was obtained. 136g [Ba/Ti(mole ratio) =1.4] of a barium hydroxide and 8 monohydrates is added in this suspension solution, and it was made to react for 4 hours, carrying out a temperature up and flowing back from 20 degrees C to 100 degrees C, in 0.75 hours.

[0105] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.69-1.03 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.86 micrometers.

[0106] hydroxylation titanium cake [produced in the example 3 example 1 -- in the aqueous solution which distributed I]200g uniformly by 751g of water, 82g [H₂ O₂ / TiO₂ = (mole ratio) 2.35] addition of hydrogen peroxide solution was done 30%, and the slurry whose titanium oxide concentration is 0.312 mols/l. like an example 1 was obtained

[0107] The obtained slurry was mixed to homogeneity at 60 degrees C for 2 hours, and the suspension solution was obtained. It was made to react for 4 hours, carrying out a temperature up and flowing back to 100 degrees C, in 0.5 hours adding and carrying out the nitrogen flow of the 136g [Ba/Ti(mole ratio) =1.4] of the barium hydroxide and 8 monohydrates into it, after cooling this suspension solution to 40 degrees C.

[0108] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.58-0.70 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.64 micrometers.

[0109] hydroxylation titanium cake [produced in the example 4 example 1 -- in the aqueous solution which distributed I]200g uniformly by 80g of water, 221g [H₂ O₂ / TiO₂ = (mole ratio) 6.35] addition of hydrogen peroxide solution was done 30%, and the slurry whose titanium oxide concentration is 0.75 mols/l. was obtained

[0110] The obtained slurry was mixed to homogeneity at 20 degrees C for 2 hours, and the suspension solution [III] was obtained. 116g [Ba/Ti(mole ratio) =1.2] of a barium hydroxide and 8 monohydrates is added in this suspension solution, and it was made to react for 4 hours, carrying out a temperature up and flowing back from 20 degrees C to 100 degrees C, in 0.75 hours.

[0111] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.27-0.43 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.35 micrometers.

[0112] Drawing 2 is an electron microscope photograph 30,000 times the scale factor of this which shows the particulate structure of the true spherical barium titanate manufactured according to this example 4, and drawing 3 is an electron microscope photograph 100,000 times the scale factor of this which shows the particulate structure of the true spherical barium titanate manufactured according to the example 4.

[0113] The true spherical barium titanate of this example 4 is understood that the true **** of a particle shape is high, and the particle diameter also has it, and particle size

distribution are [the ****] narrow even when it expands by 100,000 times. [almost uniform]

[0114] 194g [Ba/Ti(mole ratio) =2.0] of a barium hydroxide and 8 monohydrates was added in the same suspension solution [III] as what was produced in the example 5 example 4, after that, the same operation as an example 4 was performed, and the barium titanate was obtained.

[0115] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.15-0.25 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.20 micrometers.

[0116] hydroxylation titanium cake [produced in the example 6 example 1 -- in the aqueous solution which distributed I]100g uniformly by 2295g of water, 111g [H₂O₂ / TiO₂ = (mole ratio) 6.35] addition of hydrogen peroxide solution was done 30%, and the slurry whose titanium oxide concentration is 0.06 mols/l. was obtained

[0117] The obtained slurry was mixed to homogeneity at 20 degrees C for 2 hours, and the full lysis aqueous solution of the peroxide of titanium was obtained. 194g

[Ba/Ti(mole ratio) =4.0] of a barium hydroxide and 8 monohydrates is added in this aqueous solution, and it was made to react for 4 hours, carrying out a temperature up and flowing back from 20 degrees C to 100 degrees C, in 0.75 hours.

[0118] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.45-0.83 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.64 micrometers.

[0119] It was made to react for 4 hours, carrying out a temperature up to 100 degrees C in 0.5 hours, and flowing back at 100 degrees C, after adding 136g [Ba/Ti(mole ratio) =1.4] of a barium hydroxide and 8 monohydrates at 20 degrees C in the same suspension solution [II] as what was produced in the example 7 example 1, carrying out a temperature up to 60 degrees C in 0.25 hours and carrying out a digestion reaction at 60 degrees C for 3 hours.

[0120] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.63-0.77 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.70 micrometers.

[0121] It was made to react for 4 hours, carrying out a temperature up to 100 degrees C in 0.25 hours, and flowing back at 100 degrees C, after adding 136g [Ba/Ti(mole ratio) =1.4] of a barium hydroxide and 8 monohydrates at 20 degrees C in the same suspension solution [II] as what was produced in the example 8 example 1, carrying out a temperature up to 80 degrees C in 0.5 hours and carrying out a digestion reaction at 80 degrees C for 3 hours.

[0122] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 1.22-1.82 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle

diameter was 1.52 micrometers.

[0123] 96g [Ba/Ti(mole ratio) =0.99] of a barium hydroxide and 8 monohydrates is added at 20 degrees C in the same suspension solution [II] as what was produced in the example 9 example 1. It was made to react for 6 hours, adding 42g [Ba/Ti(mole ratio) =0.41] of a barium hydroxide and 8 monohydrates further, carrying out a temperature up from 80 degrees C to 100 degrees C in 0.25 hours, and flowing back at 100 degrees C, after carrying out a temperature up to 80 degrees C in 0.5 hours and carrying out a digestion reaction at 80 degrees C for 3 hours. The total amount of a barium hydroxide and 8 added monohydrate is 138g, and this is equivalent to 1.4 by the mole ratio of barium to titanium, i.e., [Ba/Ti], (mole ratio).

[0124] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.03-0.1 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.34-0.62 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.48 micrometers.

[0125] After lowering the same suspension solution [II] as what was produced in the example 10 example 1 to 40 degrees C by natural air cooling, 87g [Ba/Ti(mole ratio) =0.9] of a barium hydroxide and 8 monohydrates is added in it. 49g [Ba/Ti(mole ratio) =0.5] of a barium hydroxide and 8 monohydrates is added further, and it was made to react, after carrying out a temperature up and carrying out a digestion reaction to 80 degrees C for 2 hours in 0.5 hours, carrying out a nitrogen flow, carrying out a temperature up and flowing back to 100 degrees C, immediately, for 4 hours.

[0126] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.03-0.1 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.63-0.77 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.70 micrometers.

[0127] 809g of water distributes I]200g uniformly. hydroxylation titanium cake [produced in the example of comparison 1 example 1. -- Carry out [1.] titanium oxide concentration in 0.312 mols / , and 136g [Ba/Ti(mole ratio) =1.4] of a barium hydroxide and 8 monohydrates is added at 20 degrees C in this aqueous solution. It was made to react for 4 hours, carrying out a temperature up to 100 degrees C in 0.25 hours, and flowing back at 100 degrees C, after carrying out a temperature up to 60 degrees C in 0.25 hours and carrying out a digestion reaction at 60 degrees C for 3 hours, carrying out a nitrogen flow.

[0128] Thus, the obtained barium titanate was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, although 90% number distribution particle diameter by the electron microscope observation was 0.14-0.42 micrometers and the mean particle diameter was 0.28 micrometers, a particle diameter was not fixed and the configuration was oval, and it was far from the true sphere.

[0129] Drawing 4 is an electron microscope photograph 30,000 times the scale factor of this which shows the particulate structure of the barium titanate manufactured by this example 1 of a comparison. As shown in this drawing 4 , the particle diameter of the barium titanate manufactured by the example 1 of a comparison was not fixed, and its configuration was oval, and it was far from the true sphere.

[0130] hydroxylation titanium cake [produced in the example of comparison 2 example 1 -- 809g of water distributed I]200g uniformly, and concentration of titanium oxide was carried out [1.] in 0.312 mols /

[0131] A temperature up is carried out to 100 degrees C in 0.5 hours, adding and carrying out the nitrogen flow of the 136g [Ba/Ti(mole ratio) =1.4] of the barium hydroxide and 8 monohydrates to this aqueous solution at 20 degrees C, and it was made to react for 4 hours, flowing back at 100 degrees C.

[0132] Although the obtained barium titanate was the floc which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.08-0.16 micrometers and the mean particle diameter was 0.12 micrometers, the configuration was oval and was far from the true sphere.

[0133] The bottom of an ordinary pressure, and after carrying out a digestion reaction at 100 degrees C for 4 hours, it puts into an airtight container, and the temperature up was carried out and it was made to have added 136g [Ba/Ti(mole ratio) =1.4] of a barium hydroxide and 8 monohydrates at 20 degrees C in the same suspension solution [II] as what was produced in the example 11 example 1, to have carried out the temperature up at uniform velocity over 0.75 hours to 100 degrees C, and to react to 180 degrees C under pressurization for

[0134] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.05-0.1 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.63-0.77 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.70 micrometers. Moreover, this floc was very precise.

[0135] 136g [Ba/Ti(mole ratio) =1.4] of a barium hydroxide and 8 monohydrates was added in the same suspension solution [II] as what was produced in the example 12 example 1 at 20 degrees C, the temperature up was carried out to it to 100 degrees C in 0.75 hours, and it was made to react to it at 100 degrees C after that for 4 hours.

[0136] A slurring is again carried out with 1000g water, and after adding 200g of a barium hydroxide and 8 monohydrates to this slurry and mixing to it, it put into the airtight container, the temperature up was carried out to 180 degrees C in 1 hour, and it was made to have filtered and rinsed the obtained barium titanate and to react at 180 degrees C after that for 4 hours.

[0137] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.05-0.1 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.63-0.77 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.70 micrometers.

[0138] After having added 410g of ureas, and 4000g of water in 500g (titanium 16.4% inclusion) of the example 13 titanium-tetrachloride aqueous solutions and mixing in them, the temperature up was carried out, hydrolysis was performed for 4 hours, flowing back, and the slurry of the particle water titanium oxide with anatase structure was obtained.

[0139] The obtained slurry was filtered and rinsed and the anatase type water titanium oxide cake whose titanium oxide concentration is 21.0% in the equivalent weight by ignition loss was obtained.

[0140] 420g [$\text{H}_2\text{O}_2 / \text{TiO}_2 = (\text{mole ratio}) 7.06$] addition of hydrogen peroxide solution was done 30% at the aqueous solution which distributed uniformly this anatase type water titanium oxide cake 200g by 1228g of water. The concentration of the titanium oxide in the obtained slurry calculated 70% of hydrogen peroxide solution with water 30%, and was 0.312 mols/l.

[0141] The obtained slurry was mixed to homogeneity at 60 degrees C for 2 hours, and the suspension solution was obtained. 231.9g [$\text{Ba}/\text{Ti}(\text{mole ratio}) = 1.4$] of a barium hydroxide and 8 monohydrates is added in this suspension solution, and it was made to react for 6 hours, flowing back at 100 degrees C.

[0142] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.63-0.77 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.70 micrometers.

[0143] After having added 3904g of water, and 137g [$\text{H}_2\text{O}_2 / \text{TiO}_2 = (\text{mole ratio}) 2.35$] of 30% hydrogen peroxide solution in 500g (titanium 16.4% inclusion) of the example 14 titanium-tetrachloride aqueous solutions and mixing to homogeneity for 2 hours, it hydrolyzed with aqueous ammonia, the obtained hydroxylation titanium was filtered and rinsed, and the hydroxylation titanium cake (yellow) whose titanium oxide concentration is 13.0% in the equivalent weight by ignition loss was obtained.

[0144] 43g [$\text{H}_2\text{O}_2 / \text{TiO}_2 = (\text{mole ratio}) 1.18$] addition of hydrogen peroxide solution was done 30% at the aqueous solution which distributed this hydroxylation titanium cake 200g uniformly by 836g of water. The titanium oxide concentration in the obtained slurry was 0.312 mols/l.

[0145] The obtained slurry was mixed to homogeneity at 60 degrees C for 2 hours, and the suspension solution was obtained. 143.5g [$\text{Ba}/\text{Ti}(\text{mole ratio}) = 1.4$] of a barium hydroxide and 8 monohydrates was added in this suspension solution, and it was made to react to it at 100 degrees C.

[0146] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.63-0.77 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.70 micrometers.

[0147] It hydrolyzed by dropping 1000g of distilled water at example 15 titanium-isopropoxide 102.4g gradually, and into it, 172g [$\text{H}_2\text{O}_2 / \text{TiO}_2 = (\text{mole ratio}) 7.06$] addition of hydrogen peroxide solution was done 30%, and titanium oxide concentration was carried out in 0.312 mols/l. The temperature up of this aqueous solution was carried out to 60 degrees C, it mixed for 2 hours, and the suspension solution was obtained.

[0148] 159g [$\text{Ba}/\text{Ti}(\text{mole ratio}) = 1.4$] of a barium hydroxide and 8 monohydrates was gradually added at 20 degrees C in the obtained suspension solution, the temperature up was carried out from 20 degrees C to 100 degrees C in 0.75 hours, and reflux was performed for 4 hours.

[0149] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.44-0.60 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle

diameter was 0.52 micrometers.

[0150] The slurring was carried out with 1500g water, and the temperature up was carried out to 60 degrees C in 1 hour after filtering the true spherical barium titanate of 0.70 micrometers of the mean particle diameters obtained in the example 16 example 1 and rinsing with 3000g water, after having added 10ml of acetic acids, having adjusted pH to 8.50 and stirring at 60 degrees C for 1 hour, it filtered, and it dried, after rinsing with 3000g water.

[0151] The mole ratio of barium to the titanium of a barium titanate was set to 1.005 as a result of this processing. In addition, this mole ratio is the value determined by fluorescence X ray measurement, and the mole ratio of barium to the titanium of temporary-quenching powder is [the following and] the value determined by fluorescence X ray measurement.

[0152] The **** paddle machine ground the obtained barium-titanate powder for 1 hour, and temporary quenching was carried out at 1000 degrees C.

[0153] It was precise, and there was no sintering, 90% number distribution particle diameter by electron microscope observation was 0.49-0.91 micrometers, and the barium titanate obtained by the above-mentioned temporary quenching was a tetragonal rectangular parallelepiped-like barium titanate whose mean particle diameter is 0.70 micrometers.

[0154] After having filtered 100g of the true spherical barium titanates obtained in the example 17 example 1, drying and carrying out a slurring by 1000g of water again, the temperature up was carried out to 60 degrees C, 5ml of acetic acids was added after that, pH was adjusted to 8.80, and the digestion reaction was carried out at 60 degrees C for 1 hour, and after that, it dried, after having filtered and rinsing with 1000g water. The mole ratio of barium to the titanium of a barium titanate was set to 1.018 as a result of this processing.

[0155] After having carried out the uniform temperature up of the obtained fine particles to 20 degrees C - 1100 degrees C in 3 hours and carrying out temporary quenching at 1100 degrees C for 2 hours, uniform **** was carried out to 20 degrees C for 3 hours.

[0156] 90% number distribution particle diameter by the electron microscope observation without a sintering was 0.49-0.91 micrometers, and the barium titanate obtained by the above-mentioned temporary quenching was a tetragonal rectangular parallelepiped-like barium titanate of 0.70 micrometers of mean particle diameters.

[0157] Drawing 5 is an electron microscope 10,000 times the scale factor of this in which the particulate structure of the tetragonal rectangular parallelepiped-like barium titanate manufactured according to this example 17 is shown, and drawing 6 is an electron microscope photograph 20,000 times the scale factor of the tetragonal rectangular parallelepiped-like barium titanate manufactured according to the example 17 of this. As shown in these drawing 5 -6, the configuration was a rectangular parallelepiped-like and the tetragonal rectangular parallelepiped-like barium titanate manufactured according to the example 17 had the almost uniform particle diameter.

[0158] After the amount of yttrium added 1% of the nitric-acid yttrium to the weight of inclusion titanium in the example 18 titanium-tetrachloride aqueous solution, it hydrolyzed with aqueous ammonia, obtained yttrium inclusion hydroxylation titanium gel was filtered and rinsed, and the yttrium inclusion hydroxylation titanium cake whose titanium oxide concentration is 12.3% in the equivalent weight by ignition loss was

obtained.

[0159] 221g [H₂ O₂ / TiO₂ = (mole ratio) 6.35] addition of hydrogen peroxide solution was done 30%, and it reacted to the aqueous solution which distributed uniformly obtained yttrium inclusion hydroxylation titanium cake 200g by 654g of water like the example 1 hereafter.

[0160] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.63-0.94 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.78 micrometers.

[0161] hydroxylation titanium cake [produced in the example 19 example 1 -- 221g [H₂ O₂ / TiO₂ = (mole ratio) 6.35] addition of hydrogen peroxide solution was done 30%, and it reacted to the aqueous solution which distributed I]200g uniformly by 600g of water, and isopropyl alcohol 54g like the example 1 after that

[0162] It was the floc of the shape of a true sphere which consisted of a primary particle of 0.01-0.03 micrometers of particle diameters, 90% number distribution particle diameter by the electron microscope observation was 0.50-0.74 micrometers, the obtained barium titanate had narrow particle size distribution, and the mean particle diameter was 0.62 micrometers.

[0163] It ***ed to 20 degrees C in 3 hours after carrying out the uniform temperature up from 20 degrees C to 1000 degrees C in 3 hours after 90% number distribution particle diameter by the electron microscope observation manufactured by using a hydrogen peroxide by example 20 this invention filtered the true spherical barium titanate of 0.95 micrometers of mean particle diameters and dried by 0.85-1.05 micrometers and carrying out temporary quenching at 800 degrees C for 2 hours.

[0164] The barium titanate obtained by the above-mentioned temporary quenching did not have a sintering, it is the cubic spherical barium titanate of 0.95 micrometers of the mean particle diameters which maintained the particle diameter before temporary quenching, and it was [this cubic spherical barium titanate had narrow particle size distribution, and] excellent in dispersibility.

[0165] Drawing 7 is an electron microscope photograph 30,000 times the scale factor of this which shows the particulate structure of the cubic spherical barium titanate manufactured according to this example 20. As shown in drawing 7, even when it expanded by 30,000 times, the cubic spherical barium titanate of this example 20 had the high true **** of a particle shape, and its particle diameter was also almost uniform.

[0166] After having added 600g of water, and 233g [H₂ O₂ / TiO₂ = (mole ratio) 3.00] of 30% hydrogen peroxide solution in 200g (titanium 16.4% inclusion) of the example 21 titanium-tetrachloride aqueous solutions and mixing in them, 80g of the tetragonal barium titanates of 0.2 micrometers of mean particle diameters was added, and it stirred for 3 hours and mixed.

[0167] The heat hydrolysis reaction was performed, flowing back at 100 degrees C for 4 hours, after having added the 144g urea and carrying out a uniform temperature up to 20 degrees C - 100 degrees C next in 0.5 hours.

[0168] 1200g water is added and stirred in the barium-titanate inclusion hydroxylation titanium cake which repeats filtration and rinsing of a slurry after a reaction, and was obtained, and it was made to react for 4 hours, flowing back at 100 degrees C, after

carrying out a digestion reaction at 50 degrees C for 2 hours, adding and carrying out the nitrogen flow of the 302g [Ba/Ti(mole ratio) =1.4] of the barium hydroxide and 8 monohydrates into it.

[0169] The obtained barium titanate was the floc of the shape of a true sphere which consisted of a primary particle of 0.03-0.1 micrometers of particle diameters except the tetragonal barium titanate which the interior was made to contain, crystallinity was excellent, 90% number distribution particle diameter by electron microscope observation was 0.20-0.36 micrometers, this floc had narrow particle size distribution, and the mean particle diameter was 0.28 micrometers.

[0170] Drawing 8 is an electron microscope photograph 50,000 times the scale factor of this which shows the particulate structure of the true spherical barium titanate manufactured according to this example 21. As shown in this drawing 8, even when the true spherical barium titanate manufactured according to the example 21 is expanded by 50,000 times, the true **** of a particle shape is high, and the particle diameter is also almost uniform, and it turns out [of particle size distribution] that it is narrow.

[0171] After having added 600g of water in 200g (titanium 16.4% inclusion) of the example 22 titanium-tetrachloride aqueous solutions and mixing to homogeneity for 1 hour, 80g of the tetragonal barium titanates of 0.8 micrometers of mean particle diameters was added, and it stirred for 3 hours and mixed.

[0172] After that, next, 5% aqueous ammonia was gradually added until pH of liquid was set to 7, and 1000g water was added and stirred in the barium-titanate inclusion hydroxylation titanium cake which repeats filtration and rinsing and was obtained, and 200g [H₂O₂ / TiO₂ = (mole ratio) 2.58] addition of hydrogen peroxide solution was done 30%, and it stirred at 60 degrees C for 2 hours.

[0173] It was made to react for 4 hours, flowing back at 100 degrees C, after carrying out a digestion reaction at 60 degrees C for 2 hours, adding and carrying out the nitrogen flow of the 302g [Ba/Ti(mole ratio) =1.4] of the barium hydroxide and 8 monohydrates into it after cooling the obtained slurry to 20 degrees C.

[0174] The obtained barium titanate was the floc of the shape of a true sphere which consisted of a primary particle of 0.03-0.1 micrometers of particle diameters except the tetragonal barium titanate which the interior was made to contain, it excelled in crystallinity, 90% number distribution particle diameter by electron microscope observation was 0.78-1.06 micrometers, this floc had narrow particle size distribution, and the mean particle diameter was 0.92 micrometers.

[0175] 136g [Ba/Ti(mole ratio) =1.4] of a barium hydroxide and 8 monohydrates was added in the same suspension solution [II] as what was produced in the example of comparison 3 example 1 at 20 degrees C, the uniform temperature up was carried out to it to 180 degrees C in the airtight container in 0.75 hours, and it was made to react to it at 180 degrees C after that for 4 hours. The obtained barium titanate was the particle of 0.02-0.1 micrometers of particle diameters.

[0176] After having added 600g of water in 200g (titanium =16.4% inclusion) of the example 23 titanium-tetrachloride aqueous solutions and mixing to homogeneity for 1 hour, zirconic acid barium of 0.8 micrometers of mean particle diameters manufactured by solid phase technique 80g was added, and it stirred for 3 hours and mixed.

[0177] Next, 5% ammonium water was gradually added until pH of liquid was set to 7, and after that, after adding and stirring 1000g water in the zirconic acid barium inclusion

titanium oxide cake which repeats filtration and rinsing and was obtained, 200g [H₂O₂/TiO₂ = (mole ratio) 2.58] addition of hydrogen peroxide solution was done 30%, and it stirred at 60 degrees C for 2 hours.

[0178] It was made to react for 4 hours, flowing back at 100 degrees C, after carrying out a digestion reaction at 60 degrees C for 2 hours, adding and carrying out the nitrogen flow of the 302g [Ba/Ti(mole ratio) =1.4] of the barium hydroxide and 8 monohydrates into it after cooling the obtained slurry to 20 degrees C.

[0179] The obtained zirconic acid barium inclusion barium titanate was the floc of the shape of a true sphere which consisted of a primary particle of 0.03-0.1 micrometers of particle diameters except the zirconic acid barium which the interior was made to contain, it excelled in crystallinity, 90% number distribution particle diameter by electron microscope observation was 0.78-1.06 micrometers, this floc had narrow particle size distribution, and the mean particle diameter was 0.92 micrometers.

[0180] When the barium titanate of marketing manufactured by example of comparison 4 wet method was observed with the electron microscope, it was 0.1 micrometers, and the mean particle diameter had many sinterings, and was uneven form grain as which collapse grain is regarded.

[0181] Drawing 9 is an electron microscope photograph 100,000 times the scale factor of this which shows the particulate structure of the barium titanate of this example 4 of a comparison. As shown in drawing 9, the barium titanate of this example 4 of a comparison is understood that there are many sinterings and a grain form is uneven.

[0182] Although the mean grain type was 0.8 micrometers, and there were many sinterings and they were tetragonal barium titanates when the barium titanate of marketing manufactured by example of comparison 5 solid phase technique was observed with the electron microscope, the configuration was unfixed and was the large grain of particle size distribution.

[0183] Drawing 10 is an electron microscope photograph 10,000 times the scale factor of this which shows the particulate structure of the barium titanate of the example 5 of a comparison. The tetragonal rectangular parallelepiped-like barium titanate manufactured according to the example 17 of this invention shows the characteristic feature which was excellent also in which points, such as little of a configuration, particle size distribution, and a sintering, compared with the tetragonal barium titanate of marketing manufactured by the solid phase technique so that clearly, if this drawing 10 is compared with drawing 5 (drawing 5 is an electron microscope photograph 10,000 times the scale factor of this which shows the particulate structure of the tetragonal rectangular parallelepiped-like barium titanate manufactured according to the example 17 of this invention).

CLAIMS

[Claim]

[Claim 1] The true spherical barium titanate of 0.2-5 micrometers of the particle diameters which consisted of a primary particle of 0.005-0.1 micrometers of particle diameters. However, the particle diameter of the primary particle is 1/3 or less [of the particle diameter of a true spherical barium titanate].

[Claim 2] The spherical barium titanate which carries out temporary quenching of the true spherical barium titanate of claim 1 publication, and was obtained.

[Claim 3] The tetragonal barium titanate which carries out temporary quenching of the true spherical barium titanate of claim 1 publication, and was obtained.

[Claim 4] The spherical barium titanate which is made to carry out hydrothermal reaction of the true spherical barium titanate of claim 1 publication under pressurization, and was obtained.

[Claim 5] The true spherical barium titanate of 0.2-5 micrometers of the particle diameters which contain different particle-diameter grain or different composition grain inside.

[Claim 6] The manufacture technique of the true spherical barium titanate the claim 1 publication characterized by adding a hydrogen peroxide and carrying out the wet reaction of a titanium compound and the barium compound.

[Claim 7] The manufacture technique of the true spherical barium titanate claim 6 publication that a titanium compound is hydroxylation titanium or titanium oxide, and a barium compound is characterized by mixing hydroxylation titanium or titanium oxide, and a hydrogen peroxide, and carrying out a wet reaction under a barium hydroxide and an ordinary pressure after that by the barium hydroxide.

[Claim 8] The manufacture technique of a true [of the claim 7 publication whose digestion reaction temperature is 40-100 degrees C in 0.1-10] spherical [the concentration of a titanium compound / the mole ratios / as opposed to titanium in 0.01-2.5 mols/l. / of barium are 0.8-10 in a titanium oxide conversion, and / the mole ratio of a hydrogen peroxide to a titanium compound] barium titanate.

[Claim 9] The manufacture technique of the true spherical barium titanate the claim 7 publication characterized by making it react above the temperature which a reaction completes in 4 hours after a reaction carries out a digestion reaction 0.1 hours or more between the temperature completed in 4 hours, and temperature lower 50 degrees C than the temperature.

[Claim 10] The manufacture technique of the true spherical barium titanate of 0.2-5 micrometers of the particle diameters characterized by carrying out hydrothermal reaction of the true spherical barium titanate of claim 1 publication under pressurization.

[Claim 11] The manufacture technique of the tetragonal barium titanate characterized by adjusting the mole ratio [as opposed to titanium for the true spherical barium titanate of claim 1 publication] of barium to 0.95-1.05, and carrying out temporary quenching at 900-1300 degrees C.